Final Technical Report

PROCESS DEVELOPMENT FOR PRODUCTION OF COAL/SORBENT PELLETS

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Project Title: PROCESS DEVELOPMENT FOR PRODUCTION OF COAL/SORBENT PELLETS

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ABSTRACT

Each year in Illinois, a significant quantity of fine coal is disposed of because there is a limited market for fine coal. The objective of this work was to develop an economical method of pelletizing this fine coal with calcium hydroxide, a sulfur capturing sorbent, to produce a fuel which will burn in compliance with future sulfur dioxide emission levels. To potentially decrease binder costs, carbonation, which is the reaction of calcium hydroxide with carbon dioxide to produce calcium carbonate, was investigated as a method for improving pellet quality. The calcium carbonate formed can act as a cementitious binding matrix. Two potential combustion options were considered - fluidized-bed combustors (FBC's) and industrial stoker boilers.

Pelletization studies were performed using a minus 28 mesh fine coal concentrate collected from a southern Illinois preparation plant. Test results indicate that carbonation significantly improved pellet compressive strength, impact and attrition resistance, and essentially "weatherproofed" pellets formed with 5 to 10% calcium hydroxide. A common binder used for fine coal, corn starch, did not "weatherproof" pellets.

For combustion tests conducted at 850 °C, a temperature in the range of operation of FBC's, sulfur capture of 72.7% was attained for carbonated pellets formed with 10% calcium hydroxide. At this level of sulfur capture, the pellets would burn in compliance with the year 2000 limit on sulfur dioxide emissions of 1.2 pounds per million Btu. At 1350 °C, a temperature often associated with stoker boiler operation, sulfur captures were less than 5%. However, evidence gathered using a quadrupole gas analyzer to monitor sulfur dioxide emissions indicated that initially sulfur capture was appreciable, but this sulfur was released with continued exposure to high temperature. In plant-scale stoker tests of coal/sorbent pellets conducted by others, sulfur captures of 45-50% have been achieved. Thus, the low sulfur capture attained at 1350 °C is less than would be expected in a stoker boiler.

EXECUTIVE SUMMARY

Modern coal mining methods generate a significant amount of coal fines that, in many cases, are not processed because there is a limited market for fine coal. The objective of this work was to develop an economical method of pelletizing these fines with calcium hydroxide, a sulfur capturing sorbent, to produce a readily-transportable fuel which will burn in compliance with future sulfur dioxide emissions limits. Either fluidized-bed combustors or stoker boilers are anticipated to be markets for these pellets.

When coal is pelletized with a sulfur capturing sorbent, a binder such as corn starch or asphalt is routinely used to produce pellets with sufficient integrity to withstand handling and transportation. To decrease binder costs, the process of carbonation was investigated as a method for reducing the need for these relatively expensive binders. Carbonation is the reaction of calcium hydroxide with carbon dioxide to produce a bonding matrix of calcium carbonate. The rate of reaction is slow at atmospheric levels of carbon dioxide (0.033%) but increases dramatically at higher concentrations.

Moisture content is also a critical factor influencing the rate of carbonation. Moisture is required for the reaction to occur. However, if too much moisture is present in a pellet, the pore spaces are filled and carbon dioxide must diffuse through the water to reach the calcium hydroxide and react. This severely slows the reaction. The ideal situation is when there is just enough moisture to coat the calcium hydroxide allowing for the reaction to proceed.

The research consisted of three tasks. In task 1, the objective was to investigate carbonation as a method to improve pellet quality using a fine coal concentrate collected from an Illinois preparation plant. In task 2 (combustion), the objective was to determine sulfur capture of coal/calcium hydroxide pellets. In task 3 (process integration), the objective was to develop process oriented information for production of coal/calcium hydroxide pellets.

The fine coal concentrate used in this study was obtained from a south-central Illinois preparation plant. The sample was mined from the Illinois No. 6 seam and was moderately high in sulfur at 2.62% with an ash content of 10.8%. Microtrac analysis of the sample indicated a mean particle size of 231 microns (approximately 60 mesh) and a 90% passing size of 554 microns (approximately 28 mesh). The sample was obtained after it was dewatered at the plant by a screen bowl centrifuge to a moisture content of approximately 20% by weight. After collection, the sample was stored in sealed containers to guard against moisture loss.

The results from pelletization testing indicate that carbonation shows significant promise as a method for binding Illinois coal fines. Carbonated pellets containing 10% calcium hydroxide achieved a cured compressive strength (strength after drying) and attrition and impact resistance equivalent to pellets formed with 1.75% corn starch. Results for green strength (strength before drying) and most importantly, weatherability, were far superior to those obtained using corn starch. Pellets formed with 1.75% corn starch disintegrated soon after immersion in water while carbonated pellets formed with 10% calcium

hydroxide maintained a compressive strength after 24 hours of immersion in water nearly equivalent to the green strength. Non-carbonated pellets formed with 10% calcium hydroxide also disintegrated when immersed in water. Respective binder costs for the pellets containing 1.75% corn starch and 10% calcium hydroxide were $4.75 and $6.10 per ton of pellets produced.

Also, of importance is the fact that for combustion tests conducted at 850 ° C, a temperature in the range of operation for fluidized-bed combustors, the pellets bound with corn starch attained only 6.9% sulfur capture while the carbonated pellets containing 10% calcium hydroxide retained 72.7% sulfur in ash. At this level of sulfur capture, the pellets would burn in compliance with the year 2000 sulfur dioxide emissions limit of 1.2 pounds per million Btu. Also, chlorine emissions for this relatively high chlorine coal (0.39%) were reduced approximately 20%. Thus, for comparable binder costs, a clean-burning fuel can be produced with physical characteristics (weatherability) superior to pellets bound with corn starch.

To determine process oriented information, tests were conducted to determine the effect of carbon dioxide concentration and moisture content on the rate of strength development due to carbonation. Pelletization tests were conducted using an 18% moisture, 10% calcium hydroxide feed. This is approximately the moisture level the centrifuge product would have after dilution with 10% calcium hydroxide (some moisture loss occurred while processing the feed in the laboratory). Results indicate that increased carbon dioxide content and moderate drying of the pellets (3 to 5 percentage points loss of moisture) before carbonation increased the rate of carbonation.

Generally, the carbonation rate for the pellets formed with the 18% moisture feed was very fast when a carbonating gas of 100% carbon dioxide was used with a substantial compressive strength attained in five minutes. The rate was found to decrease with reduced carbon dioxide concentration until at 10% carbon dioxide content in the carbonating gas, very little strength was developed even with a 60 minute carbonation time. However, when the pellets were dried to reduce their moisture content by 3 to 5 percentage points before carbonating, the rate of carbonation was increased substantially for carbonating gases containing lower carbon dioxide contents. This increase in rate is attributed to moisture being removed from the pores which then allowed the carbonating gas to more readily diffuse into the pellet.

For example, when pellets dried to reduce their moisture content by 5 percentage points were exposed to a carbonating gas containing 25% carbon dioxide, the rate of carbonation was superior to results obtained for non-dried pellets carbonated with a gas containing 75% carbon dioxide. In 15 minutes, pellets attained a compressive strength of approximately 100 pounds. Maximum strengths attained for 10% calcium hydroxide carbonated pellets, even with extended carbonation times, were in the range of 125-150 pounds. It is unlikely that full strength development would be required to sufficiently harden and weatherproof these pellets for handling and transportation. The pellets exposed to a 25% carbon dioxide carbonating gas for fifteen minutes were "weatherproofed". Shorter carbonation times and lower gas concentration are likely to produce the desired pellet quality based on the results to date.

Table 1 is an example of the results obtained during the contract period. Results for samples formed with no binder, 1.75% corn starch and 10% calcium hydroxide are presented. To provide pellets for combustion testing, corn starch was used to produce pellets with sufficient integrity for testing. The carbonated 10% calcium hydroxide pellets were dried to reduce their moisture content by 4% and then carbonated for 15 minutes using a gas containing 25% carbon dioxide. (The pellets tested for sulfur and chlorine capture were carbonated for one hour using 100% CO_2. These pellets attained a compressive strength of approximately 134 pounds).

Table 1. Results from pellet testing*

	Binder			
Pellet Characterization	0% Binder	Corn Starch (1.75%)	10% $Ca(OH)_2$	10% $Ca(OH)_2$, CO_2
[1]Green strength	2	9	21	98
[2]Cured strength	2	105	47	98
[3]Attrition Resistance	2	91	47	86
[4]Impact Resistance	18"-1.5	72"-8.75	18"-6.25	72"-11.4
[5]Weatherability	disintegrated <3 min	disintegrated <5 min	disintegrated <3 min	30
[6]Sulfur capture		6.9%	75.5	72.7
[6]Chlorine capture		0.0%	22.5	17.7

*All pellets were formed using a 3000 psi compaction pressure. All results except for green strength are for cured pellets. The values for compressive strength are in pounds, value in psi would be approximately 5 times greater because pellets tested are one-half inch in diameter. Carbonated pellets were carbonated for 15 minutes using a gas containing 25% carbon dioxide, CO_2 indicates a carbonated pellet.

[1] Strength after formation or after carbonation for carbonated pellets. Carbonation does not result in a significant loss of moisture content. Results reported are the average of 4 tests.

[2] Strength after drying for one-hour in a vacuum dryer set at 70 °C and 25-30 inches Hg vacuum. Results reported are the average of 4 tests.

[3] Six pellets are placed on a 20 mesh sieve and shaken for 20 minutes using a Ro-Tap sieve shaking machine. Value is percent greater than 20 mesh after 20 minutes. Pellets tested are cured pellets.

[4] Impact resistance tests are conducted by dropping pellets onto a concrete floor at specified heights and noting when a pellet breaks into two or more pieces. Chipping around the edges is not considered failure. Initial test height is 18". If a pellet survives 25 drops at this height, the height is increased to 36" and another pellet tested. If the pellet survives 25 drops at this height, a new pellet is tested at 72". Values listed are the drop height at failure and the number of drops to failure at the height. Results reported are the average of 4 tests. Pellets tested are cured pellets.

[5] Weatherability tests are conducted by immersing 4 pellets in water for 24 hours and then measuring compressive strength.

[6] Sulfur and chlorine capture for combustion tests conducted at 850 °C. Values for sulfur capture are for tests run in duplicate. Values for chlorine capture are for single runs.

OBJECTIVES

The goal of this work was to develop a process flow diagram to economically produce a clean-burning fuel from fine Illinois coal. To accomplish this, the process of pelletizing fine coal with calcium hydroxide, a sulfur capturing sorbent, was investigated. Carbonation, which is the reaction of calcium hydroxide with carbon dioxide (in the presence of moisture) to produce a bonding matrix of calcium carbonate, was investigated as a method for improving pellet quality and reducing binder costs. Proper moisture level is critical to allow the reaction to occur. If too much moisture is present in a pellet, the pore spaces are filled and carbon dioxide must diffuse through the water to reach the calcium hydroxide and react. This severely slows or stops the reaction. The ideal situation is when there is just enough moisture to coat the calcium hydroxide allowing for the reaction to proceed. The process has been successfully demonstrated on a pilot-scale as a method of hardening iron ore pellets (Imperato, 1968). Two potential combustion options were considered for the coal/calcium hydroxide pellets: fluidized-bed combustors and industrial stoker boilers.

To accomplish the project objectives, a research program consisting of the following three tasks was conducted.

1. Pellet Formation - to investigate carbonation of calcium hydroxide as a method to improve pellet quality and reduce overall binder costs. Variables to be investigated included, binder level, optimum moisture content and required carbonation time and carbon dioxide concentration.

2. Combustion - to determine sulfur capture data for both carbonated and non-carbonated pellets at temperatures of 850 °C and 1350 °C.

3. Process Integration - to develop a flow diagram optimized for both the pelletization and combustion steps.

BACKGROUND

Environmental concerns about acid rain, due in part to sulfur emission during coal combustion, have prompted research to determine methods of reducing these emissions. A method being investigated to accomplish this is the use of calcium based sorbents to act as sulfur capture agents during combustion. One application of this approach has been to mix coal with lime and some form of binder to make pellets as feedstock for industrial stoker boilers (Conkle et al., 1983; Douglas et al., 1990). Drawbacks of this approach are moderate sulfur captures for the relatively high temperature stokers and high binder costs. Recently, others have reported significant sulfur captures at lower combustion temperatures associated with fluidized-bed combustion (Rapp et al., 1990; Otaigbe and Egiebor, 1990).

Parallel to this work, advanced physical fine coal cleaning processes are being developed to more efficiently reduce inorganic (pyritic) sulfur levels prior to combustion. These fine coal cleaning processes have potential application not

only in future work to deep clean a finely ground preparation plant product, but also for recovering the fine coal (-100 mesh) currently rejected in many plant waste streams. Each year 2-3 million tons of these fines are disposed of in Illinois due to limited marketability and questions of recoverability (Bhagwat, 1989).

Waste coal fines present several advantages toward producing a clean burning fuel. One, the particle size of the coal is already quite fine and significant amounts of pyrite and other mineral matter are liberated and would be rejected by such techniques as advanced froth flotation. Two, evidence gathered at the ISGS indicates that the fines fraction from a preparation plant often has a significantly lower levels of organic sulfur than the coarse coal from the plant (Lytle, et al., 1989). This is most likely due to differences in maceral composition. Lastly, since the coal in many cases is being disposed of, mining costs are essentially zero. In fact, waste disposal costs would be lessened which would further improve process economics. The combination of these many factors indicate potential for plant waste fines as an economical clean-burning fuel source for fluidized-bed combustors and stoker boilers. This would significantly increase their marketability and help improve the overall economics of mining and processing coal.

EXPERIMENTAL

Materials

The fine coal used in this work was obtained from a south-central Illinois preparation plant. The sample was mined from the Herrin (Illinois No. 6) seam and was obtained after dewatering by a screen bowl centrifuge. The sample is a composite concentrate from the plant's flotation circuitry and a collection of spiral concentrators. After collection, the sample was stored in sealed containers to guard against moisture loss. The "as received" moisture content was approximately 20%.

The sample (see complete chemical analyses in Table 2) was moderately high in sulfur at 2.62% and had an ash content of 10.8%. Microtrac analysis of the sample indicated a mean particle size of 231 microns (approx. 60 mesh) and a 90% passing size of 554 microns (approx. 28 mesh).

The calcium hydroxide used was a commercial sample prepared from Burlington seam limestone. The corn starch tested was obtained from a commercial grain processing facility.

Procedures

Pellet Formation

Sub-samples for laboratory testing were obtained from the main source by riffling. Although the sample was relatively fine coal, the particle size was large enough and the moisture content low enough that the sample could be riffled using a conventional Jones riffler. Samples were riffled into approximately 125

gram (dry basis) batches for testing and care was taken to avoid significant moisture loss during riffling and handling.

To prepare coal/binder mixtures, the desired binder was added to the coal sample and mixed in thoroughly by hand. If moisture was to be added, it was added after this initial mixing and then the sample was further mixed to ensure even distribution of moisture.

Pellets were formed using a 1/2 inch (inside diameter) stainless steel cylindrical mold and piston and a Carver hydraulic press. Pellets formed were 1/2 inch in diameter and approximately 5/8 inches in height. Standard formation procedure was to place the sample in the mold, compact with the desired pressure for 10 seconds (unless noted otherwise), and then the pellet was removed from the mold. Because pellet height was a function of the amount of sample placed in the mold, and this varied slightly from pellet to pellet, there were slight differences in pellet height.

For each mixture, a sample was removed to obtain a moisture content before pelletization. Moisture content was determined by drying on a hot plate until no further weight loss due to evaporation was observed. Moisture content after pelletization was also determined by removing 3 pellets and drying them on the hot plate.

Pellet Carbonation

Pellets were carbonated in both static and dynamic systems. The results discussed in the Binder and Moisture Content and Pellet Characterization sections were obtained using the static system. The results in the Variable Carbonation Times and Carbon Dioxide Concentrations section were obtained using the dynamic system.

The static system consisted of a weather balloon connected to a source of pure carbon dioxide, a desiccator connected to the weather balloon and also to a vacuum line. The procedure followed was to fill the weather balloon with carbon dioxide, close the valve to the balloon, place the pellets in the desiccator, evacuate the desiccator using the vacuum line (vacuum of minus 20 mmHg), then open the valve to the weather balloon to introduce the carbon dioxide into the desiccator. Carbonation times were one hour using this procedure.

The dynamic carbonation system consisted of a 4 inch diameter Buchner funnel sealed with a No.15 rubber stopper. A 1/4 inch hole was cut into the stopper to allow the carbonating gas to escape. Inside the funnel was a wire screen mounted approximately 1/2 inch above the base of the funnel. The wire screen served as a platform to allow all portions of the pellets to be exposed to the carbonating gas. The rubber stopper used to seal the funnel was shortened by about one-half inch to provide enough room in the funnel for the pellets once the system had been sealed.

The carbonating gases consisted of mixtures of carbon dioxide and nitrogen. Total gas flow was 1000 ml/min with rotometers being used to proportion gas flow volumes. Prior to entering the carbonator, the gases were joined using a "y"

connector and, to improve mixing, passed through a cylindrical filled with ceramic rings. The tube measured 3/4 inches in diameter by 6 inches in length.

The carbonation procedure followed was to place the pellets on the wire screen platform in the funnel. The funnel was then sealed using the rubber stopper. Carbonating gases were then introduced into the funnel through the base. The gases exited the funnel through the exit line in the rubber stopper. Exit gases were passed through a flow meter to monitor total gas flow rate to ensure that there were no leaks in the system.

After pelletization and carbonation (except for determination of green strength), the pellets were dried for 1 hour using a vacuum drier set at 70 °C and with a vacuum of approximately minus 25in. Hg.

Pellet Characterization

Compressive Strength Testing - Compressive strength was measured using a Tinius-Olsen compressive strength testing machine. The planar ends of the cylindrical pellets were placed between two parallel plates, a load was applied at 0.2 inches per minute and compression to failure was recorded. The purpose of the test was to gauge the relative strength of the pellets to withstand the stress applied if positioned in a coal pile. Results reported are an average of 4 results.

> Green strength - Compressive strength after formation (or after carbonation for carbonated pellets, carbonation did not significantly lower moisture content).
>
> Cured strength - Compressive strength after drying pellets for one hour in a vacuum dryer set at 70 °C and approximately 25 inches Hg vacuum.

Attrition Resistance - For attrition resistance testing, 6 pellets were weighed, placed on a 20 mesh sieve and shaken for 20 minutes using a conventional Ro-Tap sieve shaking machine. The weight of the pellets which remained on the sieve after 20 minutes was recorded and the percent loss calculated. This test was designed to characterize the pellets resistance to abrasive forces generated during routine handling. Pellets tested were cured pellets.

Impact Resistance Testing - Drop tests were conducted by dropping pellets onto a concrete floor at specified heights and noting when an agglomerate broke into two or more pieces. Chipping around the edges was not considered failure. Initial test height was 18". If a pellet survived 25 drops at this height, the height was increased to 36" and another pellet tested. If the pellet survived 25 drops at this height, a new pellet was tested at 72". Results reported are the average of 4 tests. This test was designed to characterize the ability of a pellet to withstand a force such that would occur when dropped off a conveyer belt into a pile. Pellets tested were cured pellets.

Weatherability Testing - Weatherability tests were conducted by immersing 4 pellets in water for 24 hours and then the compressive strength was measured in the manner described previously. The purpose of this test was to determine if

a pellet could maintain its integrity if subjected to rainfall that could occur during shipping or outdoor storage.

Combustion testing

The apparatus used for combustion testing consisted of: a high-temperature furnace capable of operating at temperatures up to 1350 °C, a mullite combustion tube, a LFE computerized temperature controller, a Dycor quadruple gas analyzer (QGA) and a Compaq personal computer. A second oxidation zone (filled with CuO and held at 800 °C) was made in the mullite tube to assure that all the volatiles were oxidized during combustion to carbon dioxide and sulfur dioxide prior to exiting to the tube. The combustion furnace temperature was controlled by a thermocouple located in the center of the furnace outside of the mullite tube. A second thermocouple was positioned inside the mullite tube adjacent to the pellet to obtain a more accurate temperature profile of the pellet as it burned. As the combustion gases exited the mullite tube, a continuous sample was taken through a capillary tube (50 μm) and monitored for carbon dioxide and sulfur dioxide by the QGA. The QGA, the LFE temperature controller, and the inside thermocouple were connected to the Compaq PC which controlled the data acquisition for each combustion experiment.

Combustion tests were performed using air with a flow rate of 560 cc/min. For each test, the furnace was brought to the desired combustion temperature and the pellet placed in the furnace. (To fit into the combustion boat, the pellets used were 1/4 of the size produced with a shape approximately a quarter section of a cylinder). Combustion and monitoring of combustion gases by the QGA commenced immediately. Each test was run until the QGA output indicated carbon dioxide emissions has ceased. The residue from each combustion test was then acid leached to determine residual sulfur. Comparison of this value to the sulfur in the feed pellet, determined by ASTM methods, was used to determine sulfur capture. Chlorine capture was determined in a similar manner. Neutron Activation for chlorine content was performed on combustion residues from tests conducted at 850 ° C.

RESULTS

As noted in the Objectives section, this project consisted of three tasks; Pellet Formation, Combustion, and Process Integration. The Results section of this report represents the work for tasks one and two. The Discussion section represents the work for task three.

Binder and Moisture Content

Samples were pelletized with no binder and with 5, 10, and 15% calcium hydroxide contents (percentage of total sample weight) and using 0.5, 1.0, and 2.5% corn starch. Two moisture ranges were investigated, 17.5-20% and 22.5-24.5% (corn starch was tested at 16.0-18.6% and at 27.8%). The lower moisture level was basically the moisture level attained by dewatering using a screen bowl centrifuge. However, a slight amount of water was added to each sample to account for the dilution effect of binder addition and thus allowed the samples to be of more similar moisture contents. Corn starch was tested as a binder so the results for carbonation of pellets containing calcium hydroxide could be compared to pellets bound with a conventional binder. Corn starch has been commonly used as a binder for coal and other fines. Mixtures of calcium hydroxide and corn starch were also tested to investigate potential synergistic effects. Samples were compacted with pressures ranging from 610 to 6100 psi.

The results (see Table 3) indicate that the pellets formed with no binder have very little compressive strength, even at higher compaction pressures. Addition of calcium hydroxide was found to increase pellet strength with strength increasing as a function of increasing calcium hydroxide content. Carbonation was found to be quite effective at increasing pellet strength for the 10% and 15% calcium hydroxide samples producing increases in strength of greater than 100% (see Figure 1). For the carbonated 10% calcium hydroxide pellets (at 3050 psi compaction pressure), strength developed was more than 15 fold greater than samples formed without binder. This increase in compressive strength was consistent over a range of compaction pressures. At a 5% calcium hydroxide content, strength developed was improved over that for pellets formed without binder, but strength development due to carbonation was modest. For the carbonated samples, the greatest compressive strengths were generally observed at the lower moisture range.

For the pellets formed using corn starch as a binder, strength increased as a function of increasing corn starch concentration. The greatest strength was obtained with the 2.5% corn starch, 6100 psi, 18.6% moisture sample. However, at the low compaction pressure of 610 psi, the higher moisture sample produced pellets which had a significantly higher compressive strength (114 psi to 53 psi).

For the pellets formed from a mixture of calcium hydroxide and corn starch there is no evidence of any synergistic effects. For the most part, compressive strengths were much the same as for the pellets formed without corn starch.

The effect of compaction time on pellet strength was also investigated. For this work, a mixture of coal with 10% calcium hydroxide was prepared and pelletized using a 3050 psi compaction pressure. Compaction times of 5, 15, and 30 seconds

were investigated. The results are listed in Table 4. As may be observed, there was no apparent benefit to extended compaction times.

To determine if laboratory drying methods influenced pellet strength development, a test was conducted using two methods of drying, vacuum drying at 70 °C and with a vacuum of approximately minus 25 inches Hg, and, air drying in an air dry oven at 95 °F. The vacuum dried samples were dried for 1 and 2 hours and the air dried samples were dried for 20 hours. The results (see Table 5) indicate that the 1 and 2 hour samples exhibit similar compressive strengths while the air dried samples have slightly higher strengths. This was possibly due to the air-dried pellets carbonating while drying which resulted in an increase in strength. This could have been true for the carbonated pellet also because the pellets may not have been fully carbonated initially. To ensure that the pellets did not carbonate during drying, which could influence comparison of results, all other results reported were for samples vacuum dried for one hour at 70 °C and at approximately 25 inches Hg.

Pellet Characterization

A pellet characterization program was conducted to expand upon results discussed in the Binder and Moisture Content section. Pellets formed with two calcium hydroxide contents and one corn starch content were tested for green strength, cured strength, attrition and impact resistance and weatherability. Pellets were carbonated for one hour. The carbonated and non-carbonated pellets were prepared from different batches of feed material. However, for the corresponding carbonated and non-carbonated pellets, results are comparable to those obtained when comparing carbonated and non-carbonated pellets prepared from the same batch. Based on results obtained earlier, pellets were formed using a 3000 psi compaction pressure at the moisture content as collected (approximately 20%). Results for the test program are listed in Table 6.

Noteworthy findings of the study were as follows:

- Carbonation significantly improved both the green and cured strength of pellets formed with 10% calcium hydroxide. Moderate improvement in strength was exhibited for pellets formed with 5% calcium hydroxide.

- The carbonated pellets maintained their integrity when stored under water for 24 hours while the non-carbonated pellets and pellets formed with 1.75% corn starch dissolved within 5 minutes of immersion in water. The pellets carbonated with 10% calcium hydroxide maintained a strength almost equivalent to the green strength.

- Although the pellets bound with 1.75% corn starch attained a compressive strength of over 100 pounds after drying, the green strength of the pellets was less than 10 pounds. Carbonated pellets formed with 10% calcium hydroxide had a significantly higher green strength (54 lbs) than the corn starch bound pellets and developed a compressive strength of over 100 pounds also. The green strength is important because this is an indicator of a pellet's ability to withstand handling after formation. Quite likely, pellets formed using only corn starch as a binder will require a significant amount of drying before they could be shipped.

- Corn starch produced pellets with the best resistance to attrition.
- Carbonation and addition of corn starch both improved impact resistance (drop testing).
- Pellets formed with no binder are of very poor quality.

Variable Carbonation Times and Carbon Dioxide Concentrations

Tests were run in the dynamic carbonation system to obtain process orientated information. The results for these tests are listed in Tables 7-10 and indicate that increased carbon dioxide concentrations and partial drying of the pellets resulted in an increased rate of carbonation.

Table 7 shows baseline information relating carbon dioxide concentration to carbonation rate. These tests were performed using a feed containing 10% calcium hydroxide at approximately 18% moisture. Compaction pressure for these tests was 3000 psi. As may be observed, carbonation rate was very fast when 100% carbon dioxide was used as the carbonating gas with a compressive strength of 89 pounds attained in five minutes (It should be noted that maximum strength developed for pellets formed with 10% calcium hydroxide was determined to be in the range of 125-150 pounds). For carbonation tests performed using gases containing 75 and 50% carbon dioxide, the rate slowed to some extent and a 15 to 30 minute carbonation time was required to obtain a strength comparable to that obtained in 5 minutes when carbonating with a gas of 100% carbon dioxide.

For carbonating gases containing 10 and 25% carbon dioxide, strength developed even after 60 minutes was minimal. To determine if strength due to carbonation could be improved by reducing the moisture content of the pellets before carbonating, a test was conducted where the pellets (formed with 10% calcium hydroxide) were dried at approximately 1.5% increments of reduced moisture before carbonating for 15 minutes using a gas containing 25% carbon dioxide. The results (see Table 8) indicate a steady, significant increase in pellet strength from 62 pounds to 147 pounds crushing force as the pellets were reduced in moisture.

To further investigate the benefits of moisture reduction prior to carbonation, additional tests were conducted on pellets formed with 10% calcium hydroxide and dried to an approximate 5 percentage point moisture loss before carbonation. Carbonating gases containing 10 and 25% carbon dioxide were tested and carbonation times ranged from 5 to 60 minutes. Results are listed in Tables 9 and 10 and indicate a significant increase in pellet compressive strength for pellets carbonated using both the 10 and 25% carbon dioxide content carbonating gases. Compressive strength of 100 pounds was attained in 15 minutes for the 25% carbon dioxide carbonating gas. Compressive strengths of greater than 70 pounds were attained in 5 and 15 minutes for the carbonating gases containing 25 and 10% carbon dioxide, respectively.

Combustion Testing

Combustion tests were conducted using pellets formed with 0, 5 and 10% levels of calcium hydroxide. Tests were run at 850 °C to determine sulfur and chorine capture and at 1350 °C for sulfur capture. Both carbonated and non-carbonated pellets were tested to determine the effect of carbonation on sulfur and chlorine capture. For the pellets formed without calcium hydroxide, corn starch was used as a binder to produce a pellet with sufficient integrity for testing.

The results for sulfur capture testing at 850 °C (see Table 11) indicate that greater than 70% sulfur capture was attained for pellets formed with 10% calcium hydroxide. At 70% sulfur capture, the pellets would burn in compliance with the year 2000 compliance sulfur dioxide emission standard of 1.2 pounds per million Btu. Sulfur capture for non-carbonated pellets was slightly higher than for carbonated pellets with the non-carbonated pellets capturing 75.5% sulfur (average of 2 runs) and the non-carbonated pellets capturing 72.7% sulfur (average of 2 runs).

For pellets formed with 5% calcium hydroxide, sulfur capture was lower, as expected. Unexpectedly, the sulfur capture for the carbonated pellets was superior to that for the non-carbonated pellets. The carbonated pellets captured 38.5% sulfur (average of 3 runs) while the non-carbonated pellets captured 31.4% sulfur (average of 2 runs).

Tests were also conducted at 850 °C to determine the potential of calcium hydroxide to capture chlorine. The results are listed in Table 12 and indicate some chlorine capture for pellets containing calcium hydroxide. At 10% calcium hydroxide, the non-carbonated pellet achieved 22.5% chlorine capture and the carbonated pellet 17.7% chlorine capture.

At 1350 °C, sulfur capture was less than 5% for all pellets tested (see Table 13). This result was not unexpected because 1350 °C is above the decomposition temperature of calcium sulfate. Of interest at this temperature is the data collected using the quadrupole gas analyzer. Figures 2 and 3 shows the QGA data for the tests conducted at 850 ° and 1350 °C for the pellets formed with 0, 5, and 10% calcium hydroxide. At 850 ° there was a noticeable reduction in sulfur emissions for the pellets which contained 5% and 10% calcium hydroxide (ion current is proportional to gas partial pressure). At 1350 °C, a reduction in sulfur emissions was also noted for the pellets formed with 5% and 10% calcium hydroxide but this sulfur was released with continued exposure to high temperature.

DISCUSSION

General

The results obtained during the contract year indicate that carbonation shows significant promise as a method of binding Illinois coal fines. For the coal sample used in this year's investigation, carbonated pellets containing 10% calcium hydroxide achieved compressive strength and attrition impact resistance equivalent or superior to pellets formed with 1.75% corn starch. Results for green strength and most importantly, weatherability, were far superior to those obtained using corn starch. Pellets formed with 1.75% corn starch were determined to disintegrate soon after immersion in water while carbonated pellets formed with 10% calcium hydroxide maintained a compressive strength after 24 hours immersion in water nearly equivalent to the green strength. Non-carbonated pellets formed with 10% calcium hydroxide also disintegrated soon after immersion in water. Respective binder costs for the pellets containing 1.75% corn starch and 10% calcium hydroxide were $4.75 and $6.10 per ton of pellets.

Also of importance is the fact that for combustion tests conducted at 850 °C, a temperature in the range of operation for fluidized-bed combustors, the pellets bound with corn starch attained only 6.9% sulfur capture while the carbonated pellets containing 10% calcium hydroxide retained 72.7% sulfur in ash. At this level of sulfur capture the pellets would burn in compliance with the year 2000 sulfur dioxide emissions limit of 1.2 pounds of sulfur dioxide per million Btu. Also, chlorine emissions for this relatively high chlorine coal were reduced approximately 20%. Thus, for comparable binder costs a clean-burning fuel can be produced with physical characteristics (weatherability) superior to pellets bound with corn starch - a common binder used for coal pelletization.

Pelletization and Carbonation

A recommended process flowsheet would be to mix the calcium hydroxide with the approximately 20% moisture centrifuge product. The sample would then be sent to a pelletizer. A potentially effective pelletizer would be a California pellet mill. This is an extrusion type, or more specifically, a ring-die extrusion pelletizer. A manufacturer's representative indicated that an ideal feed to the mill would have the majority of the feed in the minus 20 mesh size range with occasional larger particles. Optimum moisture content would be approximately 20% with tolerance to 15% on the low side and 25% moisture on the high side. The particle size of the centrifuge product used in this year's research is 90% minus 28 mesh and the moisture content of feed would be approximately 19% after dilution by calcium hydroxide. Observation in the lab indicates that this feed would also pose minimal problems in feeding the mill.

During the contract period, clear trends regarding carbon dioxide contents and carbonation times were determined; namely, increased carbon dioxide contents and a moisture reduction of 3 to 5 percentage points before carbonation (when carbonating pellets prepared from the preparation plant centrifuge product) increased carbonation rate. The increased carbonation rate after partial drying is attributable to moisture being removed from the pores of the pellet which allowed the carbonating gas to more readily diffuse into the pellets. When

carbonate bonding was demonstrated on a pilot-scale (Imperato, 1968) a pelletization, drying, carbonating flowsheet was followed with the drying and carbonating being conducted in consecutive rato-louvre dryers. Cold carbon dioxide was used as a carbonating gas. However, to determine the optimum carbonation times and carbon dioxide content of the carbonating gas, an economic analyses would need to be conducted which would include consideration of the following.

1. What are the required pellet characteristics - In work performed by Battelle Columbus to produce coal/sorbent briquettes for a stoker boiler, minimal requirements for briquettes measuring 0.9x0.75x0.2 in. were a green strength of 5 psi and a set strength of 20 psi (Conkle et al., 1983). After immersion in water for 100 hours, briquettes needed to maintain a 3 psi crushing pressure. Dried briquettes needed to survive a 15 foot drop test (1 drop). The pellets prepared in this work could certainly meet such criteria, but these pellets were produced on a laboratory-scale and these are minimum requirements.

2. What quality of pellets can be produced on a large scale continuous basis? The quality of the carbonated pellet will depend upon the quality of the pellet produced by the pelletizer.

3. Can combustion gas be used as a source of carbon dioxide to simultaneously dry and carbonate the pellets? Another potential source of carbon dioxide could be kiln gas if the lime used in the pellets is calcined at the site of the preparation plant.

4. What extent of carbonation is necessary to sufficiently harden and weatherproof the pellets? The pellets may only need to be "encapsulated" by reacting the outer portion to provide a pellet with the desired characteristics.

Combustion options

Fluidized bed combustors - Fluidized bed combustion would be the recommended combustion option for these pellets. Carbonation was found to produce a high quality pellet at 10% calcium hydroxide and a moderate quality pellet at 5% calcium hydroxide. For this 2.6% sulfur sample, 5 and 10% levels of calcium hydroxide would result in a Ca/S ratio of 1.15/1 and 2.3/1.

Sulfur capture tests conducted at 850 °C, a common operating temperature for FBC's, was greater than 70%. This sulfur capture would allow these pellets to burn in compliance with the year 2000 sulfur dioxide emissions limit of 1.2 pounds per million. However, sulfur capture tests were conducted in a laboratory furnace and not a fluidized-bed combustor. Sulfur captures may be greater in a fluidized-bed combustor because sulfur escaping in one pellet may be captured by calcium remaining in another. If a higher sulfur capture was attained, pellets could be formed at a reduced calcium hydroxide content. Decreasing of calcium hydroxide to 8% would yield a 1.8/1 Ca/S ratio for these pellets (Note: For many Illinois coals, sulfur contents are in the 3-4% sulfur range. For a 3.5% sulfur coal, 10% calcium hydroxide would result in a 1.7/1 Ca/S ratio).

Stoker boilers - These pellets are not likely to be burned at compliance sulfur emissions in a stoker boiler unless steps are taken to reduce the combustion temperature.

For stoker boilers, operating temperatures, as measured by optical pyrometers, are commonly in the range of 1350 °C. The 70% sulfur capture required to achieve compliance sulfur emissions is beyond the level previously attained in plant scale testing by others such as Battelle Columbus (Conkle et al., 1983). Battelle has achieved 45-50% sulfur capture in plant-scale tests.

In combustion tests performed on this project, sulfur captures for tests performed at 1350 °C were less than 5% for all pellets tested. Output from the QGA does indicate appreciable sulfur capture for pellets formed with 10% calcium hydroxide but this sulfur is released with continued exposure to high temperature. From this information, it is apparent that, in the tests conducted by Battelle, bed temperatures were not consistently above 1350 °C or sulfur captures would have been lower.

Consolidated Coal Company (Douglas et al., 1990) has also performed some plant scale stoker tests using coal/limestone pellets. They achieved sulfur captures ranging from 25-45%. In their work it was noted that higher grate speeds led to increased sulfur capture. Higher grate speeds lead to decreased residence time in the high temperature zone. It is also important to note that for these tests the higher grate speed did not lead to a reduced level of carbon burnout.

The approach advocated by the investigators in this project is to target a low sulfur Illinois coal that needs only 45% sulfur capture or less to achieve compliance emissions in a stoker boiler. At the plant where this sample was collected, a lower sulfur #5 seam coal is also processed that the investigators feel has significant potential to produce a compliance stoker fuel. The sample has approximately 1.45% sulfur and should have similar pelletization characteristics as this year's sample because it is of similar particle size and moisture after processing.

CONCLUSIONS AND RECOMMENDATIONS

The results from pelletization testing indicate that carbonation shows significant promise as a method for hardening and weatherproofing pellets formed from fine Illinois coals and calcium hydroxide. For combustion tests conducted at 850 °C, a temperature in the range of operation for FBC's, sulfur capture of 72.7% was attained for carbonated pellets formed with 10% calcium hydroxide. For this 2.62% sulfur fine coal sample, this would produce pellets which burn in compliance with the year 2000 limit of sulfur dioxide emissions of 1.2 pounds per million Btu.

Also, although calcium carbonate is not considered to be as effective at capturing sulfur as calcium hydroxide, the results from combustion testing indicated no significant differences in sulfur capture between the carbonated and non-carbonated pellets.

Future work in this area should investigate methods to further reduce carbonation times and carbon dioxide concentrations. Also, more information needs to be gathered to properly design larger scale continuous carbonation facilities. If combustion or kiln gas can be used to simultaneously dry and carbonate the pellets, a very cost effective method of pelletization may be realized. Production of pellets on a larger scale also is an area that needs to be investigated.

Acknowledgements

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Table 2. Chemical analyses of preparation plant flotation concentrate (values are on dry basis)

Ash	10.8
Total Sulfur	2.62
Pyritic Sulfur	0.94
Organic Sulfur	1.60
Sulfatic Sulfur	0.08
Total Chlorine	0.39
Hydrogen	4.56
Carbon	73.52
Nitrogen	1.42
Oxygen	7.10
Btu/lb	12967

Table 3. Strength development as a function of compaction pressure.

		Formation Pressure (PSI)					
		610		3050		6100	
Binder System	Feed Moisture	Pellet Moisture	lbs to* Failure	Pellet Moisture	lbs to* Failure	Pellet Moisture	lbs to* Failure
no binder	20.1	15.3	2	16.4	2	15.3	16
5% $Ca(OH)_2$	18.6			14.7	36	16.8	66
5% $Ca(OH)_2$, CO_2**	18.6			14.7	47	15.3	72
15% $Ca(OH)_2$	18.6			15.2	49	13.6	68
10% $Ca(OH)_2$, CO_2	18.6			15.2	121	13.6	173
15% $Ca(OH)_2$	18.6			13.4	61	13.3	75
15% $Ca(OH)_2$, CO_2	18.6			18.4	104	13.3	207
5% $Ca(OH)_2$	23.0	20.0	2	14.7	26	18.4	42
5% $Ca(OH)_2$, CO_2	23.0	20.0	22	14.7	58	15.3	73
10% $Ca(OH)_2$	22.5	18.4	23	14.7	49	16.8	76
10% $Ca(OH)_2$, CO_2	22.5	18.4	53	18.4	104	15.3	109
15% $Ca(OH)_2$	24.2	16.8	23	17.9	26	17.0	95
15% $Ca(OH)_2$, CO_2	24.2	18.4	23	18.4	104	17.0	160
2.5% corn starch	17.2			14.7	33	18.4	58
1.0% corn starch	18.6			16.8	49	17.8	100
2.5% corn starch	18.6	16.2	53	14.7	104	16.8	245
2.5% corn starch	27.8	20.8	114	20.0	142	25.2	148
5% $Ca(OH)_2$, 0.5%CS*+*	19.4	14.9	6	14.9	80	14.8	50
5% $Ca(OH)_2$, 0.5% CS, CO_2	19.4	14.9	26	15.8	80	14.8	95
5% $Ca(OH)_2$, 0.5%CS	18.6	16.8	2	14.7	49	16.8	50
5% $Ca(OH)_2$, 1.0% CS, CO_2	19.4	14.8	22	14.3	79	14.8	103
10% $Ca()H)_2$ 1.0% CS	17.6	14.9	13	14.9	80	14.9	73
10% $Ca(OH)_2$, 1.0% CS, CO_2	17.6	13.3	63	13.9	142	13.3	185

* Value listed is in lbs, value in psi would be approximately 5 times greater because pellets tested are 1/2 inch in diameter

** CO_2 indicated carbonated pellet

+ CS indicates corn starch

Table 4. Effect of compaction time on strength development for pellets formed using 10% calcium hydroxide and a 3050 psi compaction pressure

Sample	lbs to failure**
5 sec	50
5 sec, CO_2*	138
15 sec	48
15 sec, CO_2	150
30 sec	49
30 sec, CO_2	139

* indicates carbonated pellet
** value listed is in lbs crushing force, value in psi is approximately 5 times greater because 1/2" diameter pellets used.

Table 5. Effect of drying method on strength development for 10% calcium hydroxide pellets formed with 3000 psi compaction pressure (values are averages of results from 2 batches with 3 pellets being tested from each batch at each condition).

	lbs compression to failure*
1 hr, vac dryer**	44
1 hr, vac dryer, CO_2***	128
2 hr, vac dryer	47
2 hr, vac dryer, CO_2	132
20 hrs, air dryer**	68
20 hrs, air dryer, CO_2	145

* value in psi would be approximately five times greater because 1/2" diameter pellets used
** vacuum dryer set at 70 °C and at 25-30 inches Hg vacuum
*** indicates carbonated pellet

Table 6. Results from pellet characterization testing

Binder system	Green strength	Cured strength	Weatherability	Impact resistance	Attrition resistance
binderless	8	7	disintegrated < 5 min	18°-1.5	2
5% $Ca(OH)_2$	13	23	disintegrated <5 min	18°-3.5	2
5% $Ca(OH)_2$, CO_2	25	51	4	36°-0.75	49
10% Ca(OH)	21	47	disintegrated < 5 min	18°-6.25	34
10% $Ca(OH)_2$, CO_2	54	129	47	72°-17.5	88
1.75% cornstarch	9	105	disintegrated <5 min	72°-8.75	91

Table 7. Effect of carbon dioxide concentration on strength development (≈ 18% moisture feed; 10% calcium hydroxide pellets; cured strength)

	CARBONATION TIME (MIN)				
% Carbon dioxide	0	5	15	30	60
10	38	37	38	40	48
25	29	35	41	51	64
50	35	54	83	104	132
75	29	49	70	99	134
100	37	89	96	97	121

Table 8. Effect of reduced moisture* on strength development (≈18, moisture feed, 10% calcium hydroxide pellets; cured strength, carbonating gas - 25% CO_2, 15 minute carbonation time)

% MOISTURE	COMPRESSIVE STRENGTH
16.7	62
15.4	86
13.6	114
11.9	147
10.5	129
9.2	146

Table 9 Effect of reduced moisture on carbonation rate for a carbonating gas containing 10% carbon dioxide, 10% calcium hydroxide pellets

	COMPRESSIVE STRENGTH	
Carbonation time (min)	Carbonated as formed	Dried to reduce moisture content by 6.4%
0	38	30
5	37	51
15	38	72
30	40	100
60	48	127

Table 10 Effect of reduced moisture on carbonation rate for a carbonating gas containing 25% carbon dioxide, 10% calcium hydroxide pellets

	COMPRESSIVE STRENGTH	
Carbonation time (min)	Carbonated as formed	Dried to reduce moisture content by 5.4%
0	29	43
5	35	75
15	41	101
30	51	151
60	64	150

Table 11 Sulfur capture at 850 °C for carbonated and non-carbonated pellets.

% Calcium Hydroxide	% Sulfur Capture
0	6.9
5	27.9
5	37.9
5, CO_2*	37.9
5, CO_2*	36.6
5, CO_2*	37.9
10	74.0
10	76.9
10, CO_2*	71.3
10, CO_2*	74.0

* CO_2 incidates carbonated pellet

Table 12 Chlorine capture at 850 °C for carbonated and non-carbonated pellets

% Calcium Hydroxide	% Chlorine Capture
0	0.0
5	4.5
5, CO_2*	4.5
10	22.5
10, CO_2*	17.7

* CO_2 indicates carbonated pellet

Table 13. Sulfur Capture at 1350 °C for carbonated and non-carbonated pellets.

% Calcium Hydroxide	% Sulfur Capture
0	2.0
[illegible]	1.7
5, CO_2*	2.[illegible]
10	2.6
10, CO_2*	3.2

* CO_2 indicates carbonated pellet

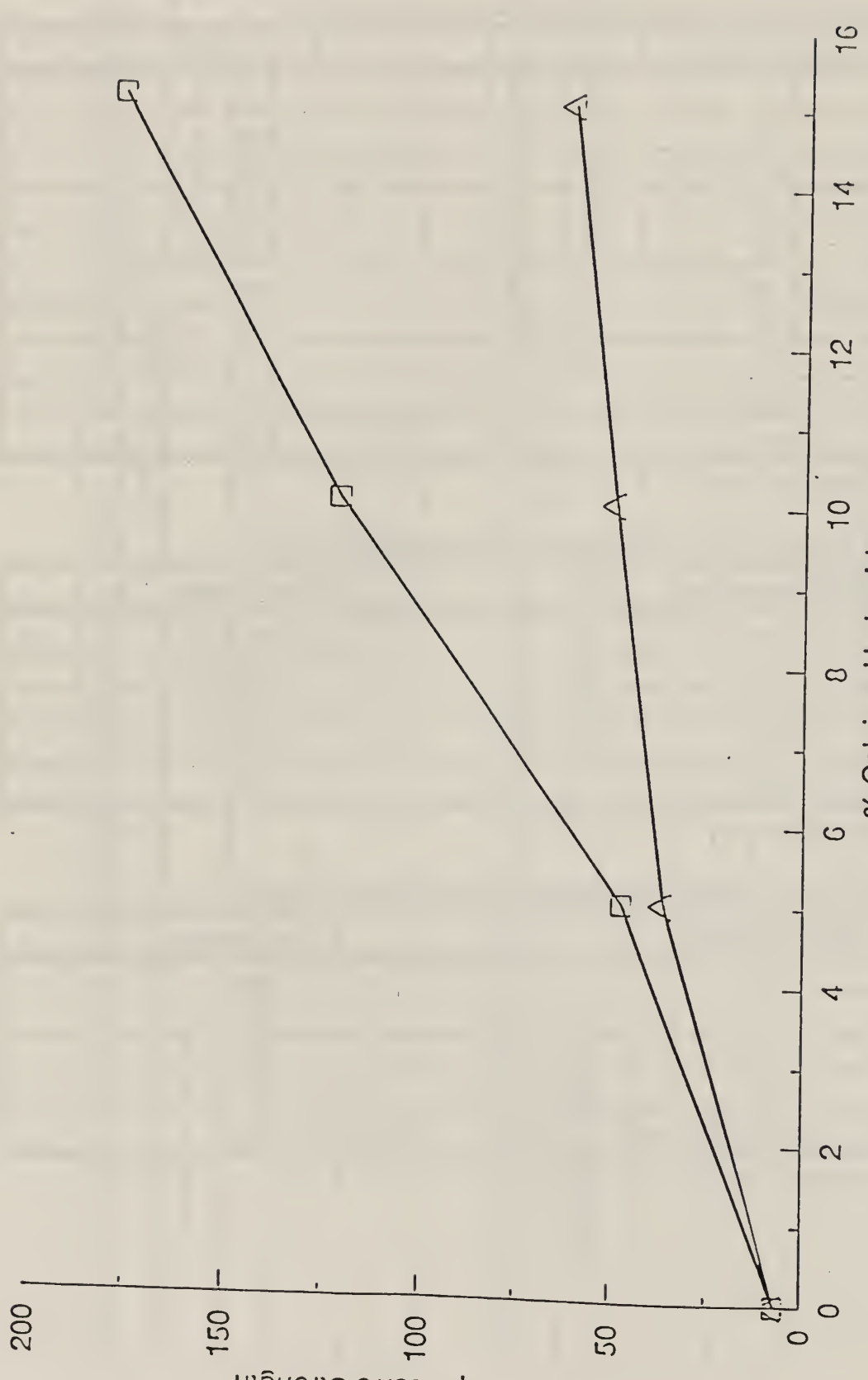

Figure 1.-Strength development due to carbonation as a function of calcium hydroxide content. Pellets were formed at 18.6% moisture content using a 3050 psi compaction pressure.

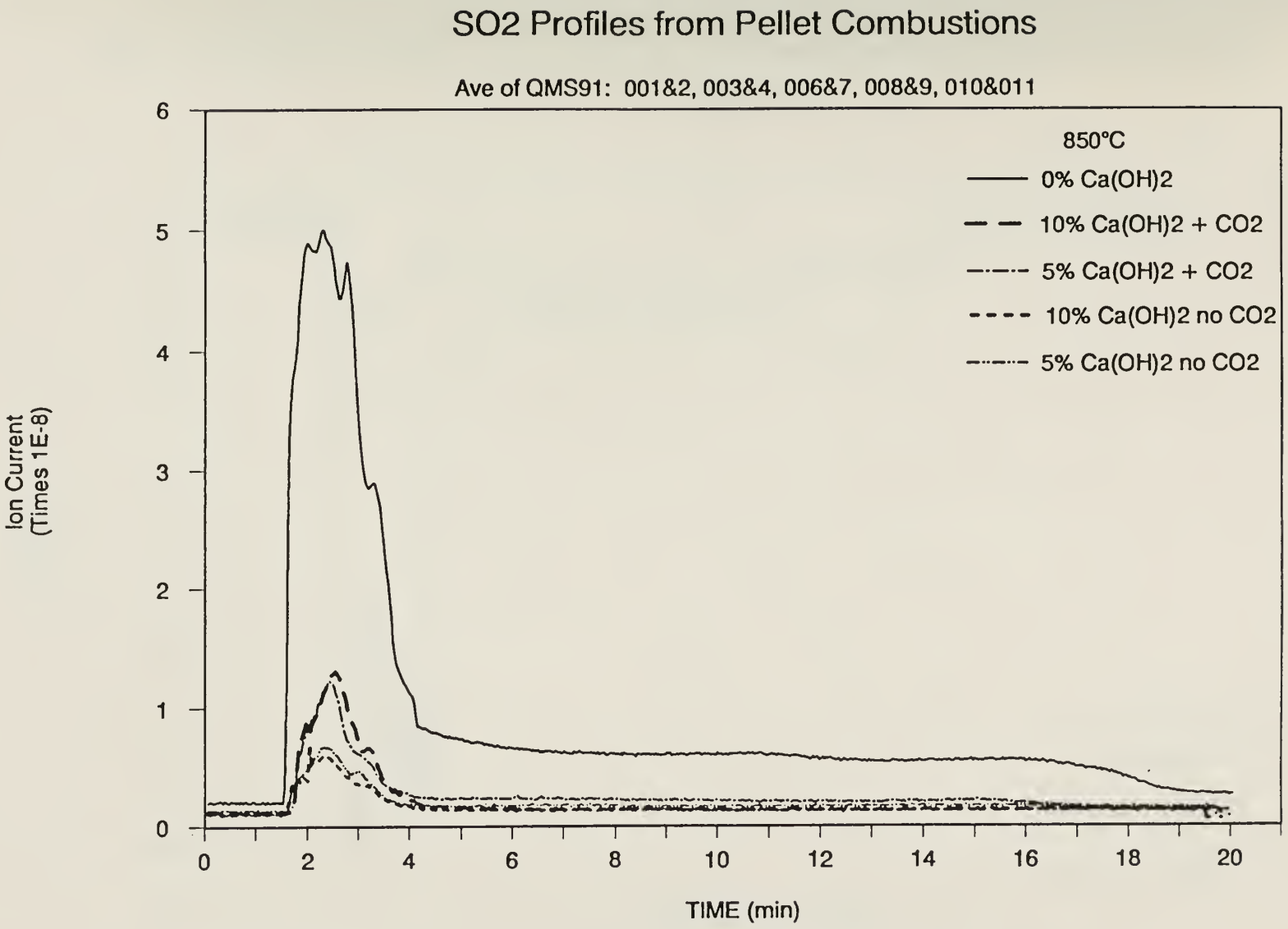

Figure 2.-QGA plot of time vs. ion current for sulfur emissions resulting from combustion of 0,5, and 10% calcium hydroxide pellets at 850°C.

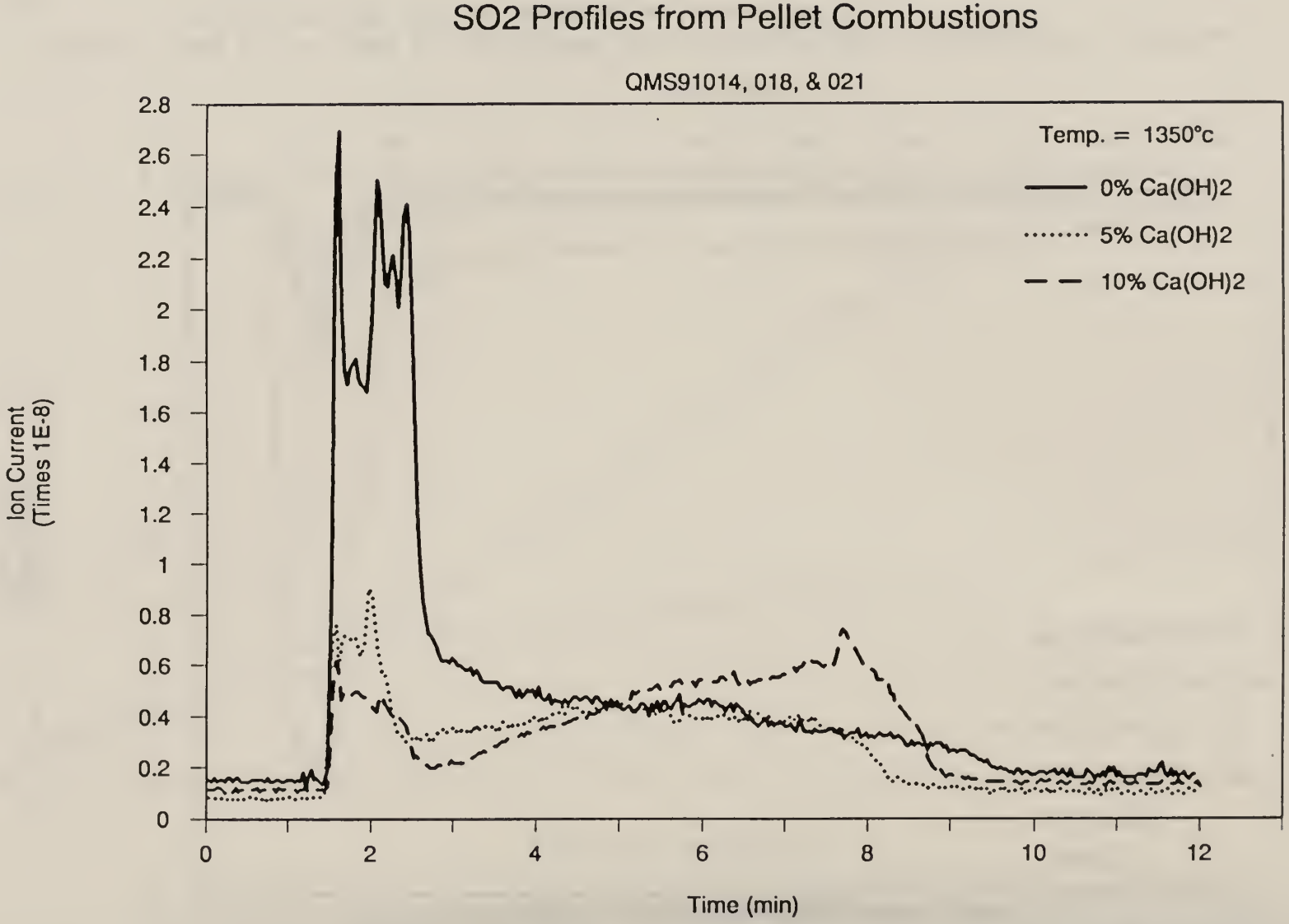

Figure 3.-QGA plot of time vs. ion current for sulfur emissions resulting from combustion of 0,5, and 10% calcium hydroxide pellets at 1350°C.